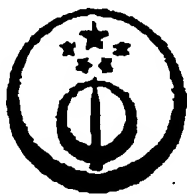


[19]中华人民共和国专利局

[11] 授权公告号 CN 1027828C



[12] 发明专利说明书

[21] ZL 专利号 92112614.X

[51]Int.Cl³

F01N 3/10

[43]授权公告日 1995年3月8日

[24]优先权 95.1.8

[21]申请号 92112614.X

[22]申请日 92.11.11

[73]专利权人 申进忠

共同专利权人 杨文毅

[72]发明人 申进忠 杨文毅

[74]专利代理机构 北京市东城区专利代理事务所

代理人 高树贤

地址 100076北京市丰台区南苑警备五路58号

B01D 53/36

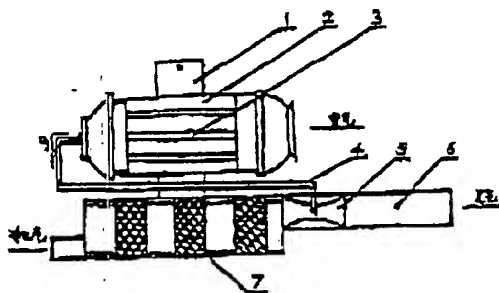
说明书页数:

附图页数:

[54]发明名称 臭氧—催化剂法汽车尾气净化器

[57]摘要

本发明涉及一种臭氧—催化剂法汽车尾气净化器。其净化器中的文丘里管与臭氧发生器的臭氧输出管连通,臭氧发生器中安装2—10根臭氧发生管,利用固定板将臭氧发生器和催化剂箱组合成一体并固定在汽车排气管处。使用本发明可以使汽车尾气达到排放的标准,不污染环境。而且净化器的结构和净化工艺均很简单,易于推广使用。



ZL92112614.X (CN1027828C)

Abstract

This invention relates to an automobile tail exhaust purifier by the method of ozone-catalyst. The Venturi tube of the purifier is connected with the ozone-outlet tube of an ozone generator. There are 2-10 ozone-generating tubes installed inside the ozone generator, and the fixed board that fixes the ozone generator with the catalyst box together is fixed on the automobile exhaust pipe. The tail exhaust can reach the ideal emission standard and do not pollute the environment by using the purifier of this invention. The purifier of this invention features a reasonable structure and simple technology. Its application is easy to be extended.

What is claimed is:

1. An automobile tail exhaust purifier by the method of ozone-catalyst, and consisted of Venturi tube and catalyst box and the like, characterized in that the Venturi tube (5) is connected with the ozone-outlet tube (4) of the ozone generator (2), several ozone-generating tubes (3) are installed inside the ozone generator, and the fixed board (1) that fixes the ozone generator (2) with the catalyst box (7) together is fixed on the automobile exhaust pipe.
2. The automobile tail exhaust purifier of claim 1, characterized in that the number of the ozone-generating tubes (3) installed inside the ozone generator (2) is 2 to 10.

An automobile tail exhaust purifier by the method of ozone-catalyst

This invention relates to an automobile tail exhaust purifier by using a two-step process combining ozone-oxidation with catalyst oxidation. This purifier is especially suitable to the purification of tail exhaust emitted by domestic automobiles using gasoline.

Presently, all domestic automobiles emit their tail exhaust directly to the atmosphere. This causes serious air pollution, especially in big cities. It is known to everybody, automobile tail exhaust contains many detrimental materials, such as: ① carbon monoxide (CO); ② oxynitride [NOx]; ③ hydrocarbon compound (HC); ④ tetraethyl-lead [Pb(C₂H₅)₄]. These materials are very poisonous and very harmful to human respiratory system, blood, liver, heart and nervous system. Now some automobiles use the catalyst method to purify tail exhaust. The main shortcoming is that the lead in the tail exhaust poisons the catalyst, decreasing the usage lifetime and needing frequent replacement of catalyst. The purification efficiency is not good.

The objective of the invention is to provide an automobile tail exhaust purifier in order to overcome the shortcomings in the existing technology. By combining ozone oxidation with catalyst oxidation, this invention solves the air pollution problem caused by automobile tail exhaust emission.

The objective of this invention is realized by the following methods:

The ozone-catalyst method automobile tail exhaust purifier consists of Venturi tube and catalyst box and the like. The Venturi tube is connected with the ozone outlet tube of the ozone generator. Several ozone-generating tubes are installed inside the ozone generator. A fixed board that fixes the ozone generator with the catalyst box together is fixed on the automobile tail exhaust pipe. The number of the ozone generating-tubes installed inside the ozone generator is 2 to 10.

Compared with existing technology, this invention has the following advantages:

Through the automobile tail exhaust purifier of this invention, the poisonous

component, such as CO, HC, NO_2 , $\text{Pb}(\text{C}_2\text{H}_5)_4$ etc. can be oxidized and become CO_2 , H_2O , NO_2 and a small quantity of organic substances with low molecules. The purifier in this invention features a reasonable structure and simple technology. After being purified by this purifier, the automobile tail exhaust can reach the ideal emission standard.

Brief Description of the drawing:

Fig.1: is a schematic diagram of the automobile tail exhaust purifier in this invention.

Fig.2 and Fig.3: are the schematic diagrams of the catalyst box with different structure.

Fig.4: is the technological process of the automobile tail exhaust purification.

The present invention is now described with reference to embodiments.

The outer cover of the automobile tail exhaust purifier by the method of ozone-catalyst, and consisted of Venturi tube and catalyst box and the like, is made of ozone-proof materials. One to twenty ozone-generating tubes (preferable two to ten) are installed inside the ozone generator. Venturi tube 5 is connected with the ozone outlet tube 4 of the ozone generator 2. The ozone-generating tubes are those produced by factories in Beijing and Shanghai etc. It is very easy for a person having ordinary skill in the art to make this kind of ozone generator.

The role of the fixed support 1 is to combine ozone generator 2 with the catalyst box 7 and the Venturi tube 5. The fixed support is fixed on an appropriate position near the tail exhaust pipe or the muffler on the automobile chassis. The fixed position near the chassis crossbeam is recommended. The fixed position can be different in different model of automobiles. The fixed support/board can be made of any sturdy materials. The commended material is carbon steel with a width of 2mm to 8mm (preferable 3mm to 5mm). The size of the fixed support/board depends on the fixed position and model of automobiles. But it must be able to support the total weight of the ozone generator and the catalyst box; it can also bear the vibration of automobile in movement. This is obvious for a person having ordinary skill in the art.

The ozone generator 2 of the automobile tail exhaust purifier of this invention produces ozone used to purify the tail exhaust of automobiles. Its structure is pipe-like. The ozone-generating tube is made of a specific glass with 5-50mm in diameter and 50-500mm in length. In its outer surface is an ozone-proof metal wire-mesh which is used to be glow discharge screen. The light tube uses a 12-24V DC source. Automobile battery or DC electric generator is used to be power supply. The outer cover of the ozone generator is made of sturdy and erosion-resistant material, metal or non-metal. Its shape can be cylinder, cube, cuboid, ellipsoid and cone etc. The working volume is 10cm^3 - 500cm^3 . The number of the ozone-generating tube 3 is determined by the tail exhaust emission quantity in different model of automobiles, generally 1-20. Usually 2-10 tubes are installed inside the generator fixed on the support, so that the air stream can flow through the surface of light tubes. The power supply socket is fixed on the outer cover of the generator. The socket is sealed, insulated and instrumental-type one. It also can be connected with the startup switch of the engine by using derivative wire. The end without connection with the ozone generator by socket is the gas-in port. One to five layers of metal wire-mesh with proper diameter of holes and one to three layers of waterproof filter cloth are installed, so that the air stream can pass through easily while the rainwater and the water on the road surface can be prevented. In the front of the light tube is a water shut-off board with semicircle shape. The condensed water inside the generator discharges from the drain cock in the lower part. In another end of the ozone generator is an active link connecting with the tail exhaust pipe through screw thread coupling or flange coupling. The active link is made of erode-resistant metals or non-metals.

The catalyst box 7 is made of high temperature-resistant and erode-resistant metals or non-metals. Its shape can be cuboid or cylinder, cube, cone and prism etc. with a volume of 0.5 liters (500cm^3) to 50 liters (50000cm^3). Inside the box are several clapboards with small holes from which the gas stream can pass through the catalyst layers fixed between the clapboards. The catalyst can also be put inside the star-like or honeycomb-shaped metal wire-mesh. The box is placed inside the outer cover. The principle of design is that the automobile tail exhaust can contact with the catalyst in extreme limitation and can pass through the catalyst layers rapidly. Considering the periodic replacement of catalyst, one end of the catalyst box should be connected by using screw thread coupling or flange coupling, so that to make

maintenance and replacement of catalyst easily. This catalyst box can both purify the automobile tail exhaust and play a role to eliminate noise. It can substitute for mufflers used in automobiles. The catalyst box can be fixed on tail exhaust pipe of the automobile engine, or placed behind the automobile muffler, depending on the automobile model and the particular position.

The role of the Venturi tube 5 is to mix ozone with automobile tail exhaust fully. The negative pressure produced by the rapid air stream makes ozone gas enter into the tail exhaust through the ozone output pipe and mix with the tail exhaust. After ozone oxidation, the mixed gas enters into the catalyst box. The Venturi tube is made of high temperature-resistant and erode-resistant metal or non-metals. Its shape can be cylinder or sphere, cuboid, cube and cone etc. The principle of design is to produce big negative pressure in the position where the ozone combines with the tail exhaust, facilitating the rapid combination of ozone with tail exhaust and the reaction of ozone oxidation.

The connection pipe 6 between the purifier and the tail exhaust outlet tube of the automobile engine uses screw thread coupling, flange coupling or long hoop. It is made of high temperature-resistant metals or non-metals. In order to prevent thermal expansion and vibration noise, the connection can also use snake spring hose. When the long hoop is used, asbestos or rubber knot (mat) should be used to prevent thermal expansion and vibration. The shape of the connection pipe and the long hoop can be cylinder, cuboid, cube and sphere etc. The size should be suitable to match the connection of Venturi tube with the tail exhaust pipe of the automobile engine. It can also use big- and-small head coupling or diameter-changeable pipe coupling, depending on the automobile model and the installation position of the purifier.

The connection pipe 6 between the ozone generator and the Venturi tube is made of ozone erode-resistant metals or non-metals with a diameter of 3mm-30mm (preferable 5mm-10mm). The length is equal to the shortest distance from the outlet of the ozone generator to the inlet of the Venturi tube. Twist should be avoided.

The automobile tail exhaust purifier used in this invention combines the ozone oxidation with catalysis. It draws advantages from ozone oxidation and catalysis oxidation and overcomes shortcomings of them. It features a long catalyst lifetime, economic cost and convenient usage.

1. Test of the ozone oxidation method

When ozone alone is used to purify the automobile tail exhaust, because the half-value period of ozone is very short, the contact time of ozone with compounds in the tail exhaust, such as CO, NO and HC etc., is very short. The output of ozone is low. The purification efficiency is poor. Besides, many intermediate ozone-oxide compounds are produced, such as methyl alcohol, formaldehyde and formic acid etc. They are poisonous substances. The automobile cannot supply the power needed for higher ozone output (see Table 1).

The content of methyl alcohol, formaldehyde and formic acid is 500 times the original one.

2. Test of catalyst oxidation method

Although catalyst can purify the tail exhaust, lead, sulfur and charcoal smoke etc. may intoxicate the catalyst, lowering the activity and purification efficiency of the catalyst, with the result that the catalyst is invalid and must be replaced within several months.

The catalyst absorbs oxygen in the automobile tail exhaust to become unstable combined state, then contacts with hydrocarbon compounds to become CO_2 . The active oxygen on the surface of catalyst is the key of purification. Because the oxygen content in automobile tail exhaust is low, which decreases the opportunity to acquire active oxygen, the activity of the catalyst and the purification efficiency. The test results are listed in Table 2.

Table 2

Series number	Consumption of catalyst	Test condition (month)	Purification efficiency of carbon monoxide %	Purification efficiency of hydrocarbon	Purification efficiency of oxynitride %
1	2kg	One month	87	85	97
2	2kg	Two months	81	87	89
3	2kg	Three months	78	81	79
4	2kg	Six months	62	47	38

3. Ozone—Catalyst method

First, the ozone transfers the highly concentrated compounds, such as CO, NO_x and HC etc., into low concentrated compounds, such as carbon monoxide, oxynitride and hydrocarbon compounds. Then after the catalysis-oxidation treatment, the automobile tail exhaust can meet the emission standard set by the state government. The lifetime of the catalyst is increased from several months to more than two years. The oxygen content in the tail exhaust increases because of the additive ozone. The adsorption ability of the catalyst to oxygen increases. The activity of catalyst enhances. Adding Mn₂O₃—Fe₂O₃ into the catalyst can prevent the catalyst from lead intoxication and enhance the vibration-resistant ability of the catalyst and increases the lifetime of the catalyst. The test results are listed in Table 3.

The ozone—catalyst combined method is a reliable and economic method used to purify automobile tail exhaust. The purification efficiency is high. The lifetime of the catalyst is long.

The following embodiments are used to explain the invention further.

Example 1.

Tail exhaust purifier for Dongfeng-style automobiles: The ozone generator is made of stainless steel of 2mm thick. The outer size is $\phi 160 \times \phi 280$. There are 4 ozone-generating tubes installed inside it. The ozone yield is 250 microgram \times 4/min.

The catalyst box is made of stainless steel of 3mm thick. The outer size is 260 \times 200 \times 100mm. Inside the box, there are 2kg of multi-component catalyst and two layers of tilt clapboard with many small holes of $\phi 2$ mm. In the rear part of the box is flange coupling (see Fig.3).

The Venturi tube is made of stainless steel. The outer size is $\phi 60 \times 80$ mm. In the throat is a $\phi 5$ mm stainless steel pipe connected by sealed bolt and nut.

The connection pipe and long hoop are made of A_3 steel. The outer size is $\phi 60 \times 140$ mm. One end is connected with the Venturi tube; another end is connected with the automobile tail exhaust pipe. In the connection position, asbestos rubber knot and long hoop are used to fix and tighten.

This automobile tail exhaust purifier is installed on the tail exhaust pipe. During the 30000km running, the content of CO, NO_x, HC and Pb(C₂H₅)₄ all reach the emission standard. The measured results are listed in Table 4.

Example 2

Tail exhaust purifier used in Toyota van: The ozone generator is made of 1.5mm thick stainless steel. The outer size is $\phi 120$ mm \times 200mm. Inside are two ozone-generating tubes. The ozone yield is 250 microgram \times 2/min.

The catalyst box is made of 1.5mm thick stainless steel. The outer size is $\phi 120 \times 300$ mm. Inside the box are two clapboards full of $\phi 10$ mm holes. The catalyst is in a $\phi 100 \times 100$ mm stainless steel wire-mesh box. The top cover in the two ends of the catalyst box uses screw thread coupling (see Fig.2).

The Venturi tube is made of stainless steel. The outer size is $\phi 50 \times 60$ mm. Inside is a $\phi 5$ mm stainless steel pipe. Screw thread coupling is used. The connection pipe is made of $\phi 5$ mm stainless steel.

The connection pipe and long hoop are made of A_3 steel. One end is welded

together with Venturi tube; another end is connected with the tail exhaust pipe of the automobile engine by flange coupling.

After 40000km running for more than one year, the tail exhaust can reach the emission standard. The test results are listed in Table 5.

Example 3

Tail exhaust purifier used in Beijing jeep:

The ozone generator is made of 5.0mm thick polyvinyl chloride. The outer size is $\Phi 120 \times 200\text{mm}$. Inside it are three ozone-generating tubes. The ozone yield is $250 \text{ microgram} \times 3/\text{min}$.

The catalyst box is made of stainless steel. The outer size is $\Phi 150 \times 300\text{mm}$. The pipe wall is 1.5mm thick. The catalyst is in a $\Phi 140 \times 50\text{mm}$ stainless steel wire-mesh box. Three $\Phi 130 \times 50\text{mm}$ stainless steel rings are used to fix the catalyst inside the catalyst box. After being purified, the tail exhaust can pass through the catalyst layers easily (see Fig.1).

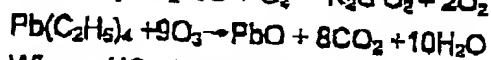
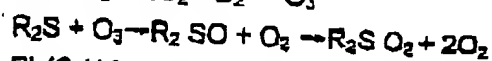
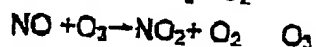
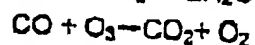
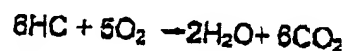
The Venturi tube is made of stainless steel pipe. The outer size is $\Phi 60 \times 80\text{mm}$. A $\Phi 5\text{mm}$ stainless steel pipe is inserted into the throat. Screw thread coupling is used. The connection pipe is made of $\Phi 5\text{mm}$ stainless steel.

The connection pipe and long hoop are made of A₃ steel. One end is connected with the Venturi tube, another end is connected with the automobile tail exhaust pipe by flange coupling.

After more than 20000km running for more than one year, the purifier is perfect. The clarifying effects are good (see Table 6).

Combining ozone oxidation with catalyst oxidation, this invention uses two-step method to purify the automobile tail exhaust. In the first step, the poisonous constituent, such as CO, HC, NO_x and Pb(C₂H₅)₄, are oxidized by ozone and become non-poisonous or low-poisonous substances. In the second step, they undergo catalysis oxidation and are transferred into CO₂, H₂O and NO₂ or small quantity of organic substances with small molecules. After being purified by this purifier, the tail exhaust can reach an ideal

emission standard. Ozone used in this invention is a three-atom allotrope of oxygen, and is obtained from ozone generator. Ozone has high oxidation potential and strong oxidation ability. It can oxidize almost organic compounds, such as hydrocarbon, sulfide, oxynitride and carbon monoxide etc. The reaction equations are as follows:



Where, HC—hydrocarbon compounds

R_2S —organic sulfide

$\text{Pb}(\text{C}_2\text{H}_5)_4$ —tetraethyl lead, a kind of antiknock materials in gasoline.

The main constituents in the multi-component catalyst used in this invention are: platinum (Pt), palladium (Pd), rhodium (Rh) and rare-earth metal oxides. They use active aluminum oxide or molecular sieve as carrier. The catalyst used in this invention can catalyze and oxidize poisonous and harmful constituents in the tail exhaust. These poisonous and harmful constituents are transferred into low poisonous or non-poisonous products, such as H_2O , CO_2 , NO_2 , P_4O etc. The catalyst used in this invention can be one of those reported in references or used in existing techniques. But it is better to make catalyst by using the method introduced here. The method is as follows:

0.01%-0.5% (weight) of platinum oxidizes with palladium, or nitrate powder (preferable 0.05%-0.15%); $[\text{Cu}_2\text{CrO}_2]$: 3-10% (weight) (preferable 5-8%); V_2O_5 : 5-15% (weight) (preferable 7-10%); Fe_2O_3 : 3-12% (weight) (preferable 5-9%); Co_3O_4 : 1-13% (weight) (preferable 4-9%); Mn_2O_3 : 1-10% (weight) (preferable 3-7%); Adding all these compounds into distilled water and mixing evenly, then adding active aluminum oxide (the catalyst carrier) or molecular sieve (preferable 4A or 5A) into the water solution above, mixing evenly and laying it aside to adsorb for 1-5 hours (preferable 1.5-2.5 hours), tipping off the water atop, put it into a furnace to activate for 2-3 hours under $300-800^\circ\text{C}$.

Technological conditions used to purify automobile tail exhaust in this invention:

1. Ozone concentration (ozone yield)

The higher the ozone concentration, the better the purification effect. However, excessive ozone will result in waste and increase power loss, cause air pollution as well. According to the emission quantity of tail exhaust and harmful constituents in tail exhaust in our country, the following ratio is used, ozone : tail exhaust = 1 : 0.5-1.5, (preferable 1 : 1 - 1 : 2). See Table 7.

2. Reaction time

The reaction between ozone and harmful constituents in tail exhaust is very rapid, 5-25 seconds between ozone and carbon monoxide, 10-25 seconds between ozone and oxynitride, 15-35 seconds between ozone and hydrocarbon, 10-20 seconds is used in this invention. See Table 8.

3. Reaction temperature

The tail exhaust purifier in this invention is suitable to a wide temperature range, especially to the start-up in low temperature. In low temperature, gasoline cannot burn completely. The contents of CO, NOx, HC etc are high. The purification effect is poor in the temperature range of 50-150°C. Using the two-step treatment method in this invention can solve this problem. In low temperature, the harmful constituents (CO, NOx, HC) can be oxidized by ozone and the concentration is lowered. Then after catalyst oxidation, the purification effect is enhanced.

Another feature of this invention is that the purification effect is still better in high temperature (300-500°C). In high temperature, the reaction between ozone and harmful constituent (CO, NOx, HC) is more rapid and more thorough. The reaction between ozone and catalyst increases the active oxygen on the surface of the catalyst and enhance the activity of the catalyst. The activity of the catalyst can regenerate and restore, increasing the lifetime of the catalyst. See Table 9.

The invented tail exhaust purifier is applicable in the temperature range of 100-500°C.

The technological process for tail exhaust purification is:

When the automobile starts up, the ozone generator 2 starts up at the same time. Air enters into the ozone generator. Under glow discharge, oxygen in the air is oxidized to become ozone (O₃). Through the ozone output pipe 4 and

Venturi tube 5, the ozone enters into the automobile tail exhaust pipe, and reacts with CO, NO, HC and $\text{Pb}(\text{C}_2\text{H}_5)_4$ etc. After ozone oxidation reaction, it enters into the catalyst purifier 7, and reacts with the multi-component catalyst to purify the harmful constituents in tail exhaust. The purification efficiency reaches 90-99%.

Table 1

Series number	Ozone concentration	Test condition	CO purification efficiency %	HC purification efficiency %	NO purification efficiency %	Remark
1	250 microgram	20km/h	74%	62%	86%	A big quantity of methyl alcohol
2	×4/min	40km/h	80%	70%	85%	Formaldehyde
3		60km/h	87%	81%	87%	

Table 3

Series number	Ozone concentration	Catalyst consumption	Test condition (year)	CO purification efficiency %	HC purification efficiency %	NO purification efficiency %
1	250	2kg	Half year	98	96	92
2	microgram /liter	2kg	One year	95	92	87
3	×4	2kg	Two year	92	89	82
4		2kg	Three year	87	82	79

Table 4

Mileage kilometer	CO purification efficiency %	NoOx purification efficiency %	HC purification efficiency %	Tetraethyl lead efficiency %
10000 kilometers	98	96	97	92
20000 kilometers	97	95	94	90
30000 kilometers	95	94	93	87

Table 5

Mileage kilometer	CO purification efficiency %	NOx purification efficiency %	HC purification efficiency %	Tetraethyl lead purification efficiency %
10000 kilometers	99	97	98	96
20000 kilometers	98	95	96	94
40000 kilometers	96	93	95	92

Table 6

Mileage kilometer	CO purification efficiency %	NOx purification efficiency %	HC purification efficiency %	Tetraethyl lead purification efficiency %
5000 kilometers	98	96	97	93
10000 kilometers	97	95	96	92
15000 kilometers	95	93	94	90
20000 kilometers	94	91	92	89

Table 7

Ozone added	CO purification efficiency %	NOx purification efficiency %	HC purification efficiency %	Remark
1:0.5	65%	72%	68%	
1:1	97%	92%	89%	
1:2	98%	95%	95%	
1:5	99%	97%	96%	

Table 8

Ozone reaction time	CO purification efficiency %	NOx purification efficiency %	HC purification efficiency %	Remark
5~10 Seconds	72%	68%	59%	
10~20 Seconds	95%	92%	91%	
20~50 Seconds	97%	94%	92%	

Table 9

Reaction temperature	CO purification efficiency %	NOx purification efficiency %	HC purification efficiency %	Remark
100~200°C	90%	89%	91%	
200~300°C	95%	94%	96%	
300~500°C	97%	96%	98%	

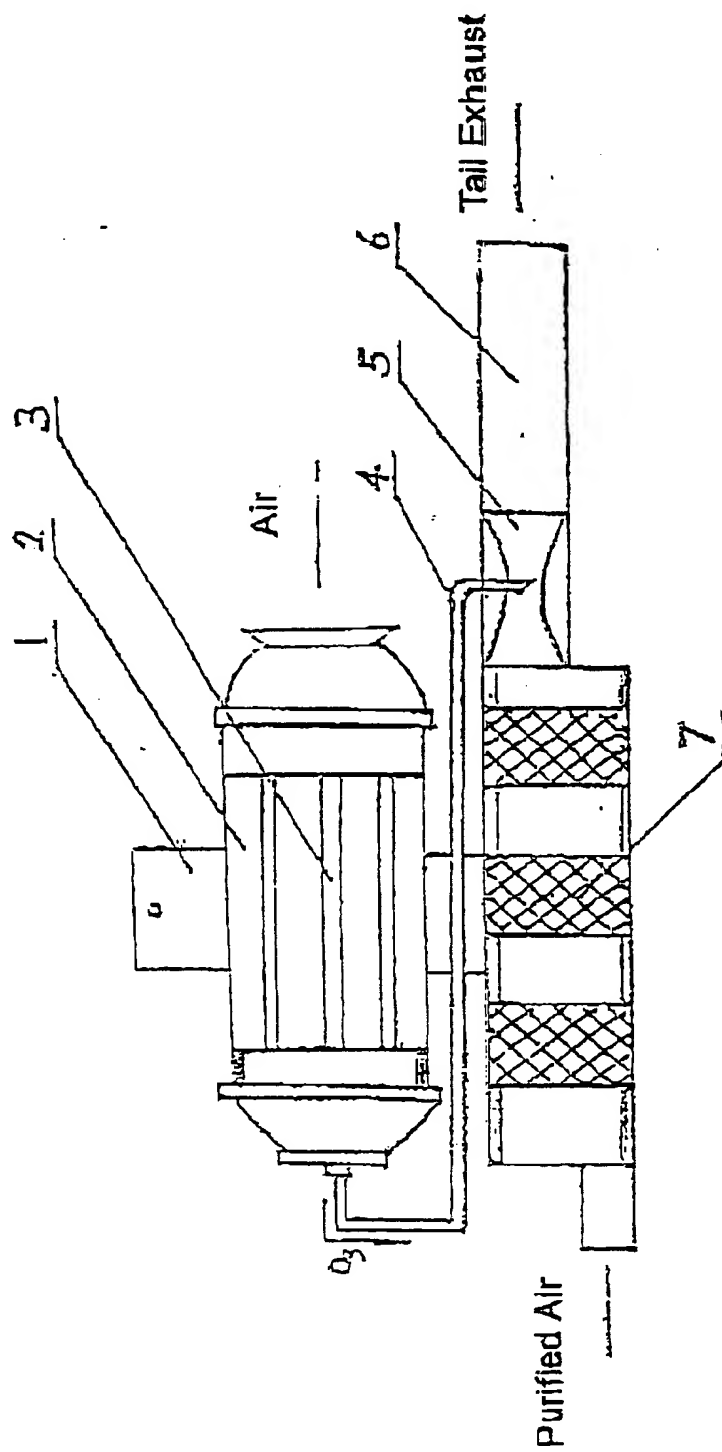


FIG 1

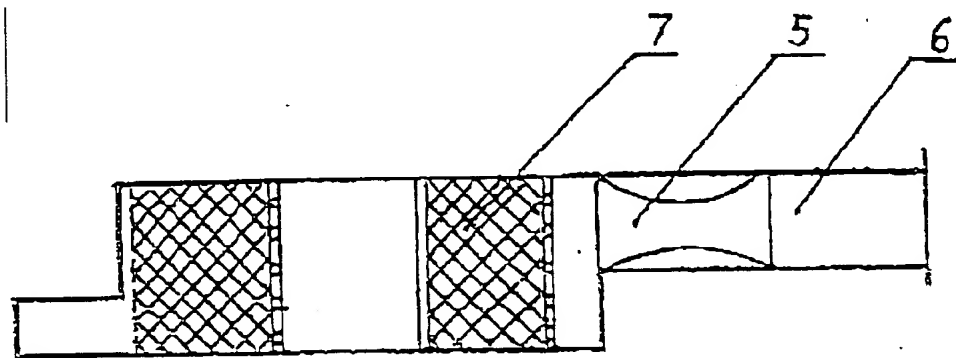


FIG 2

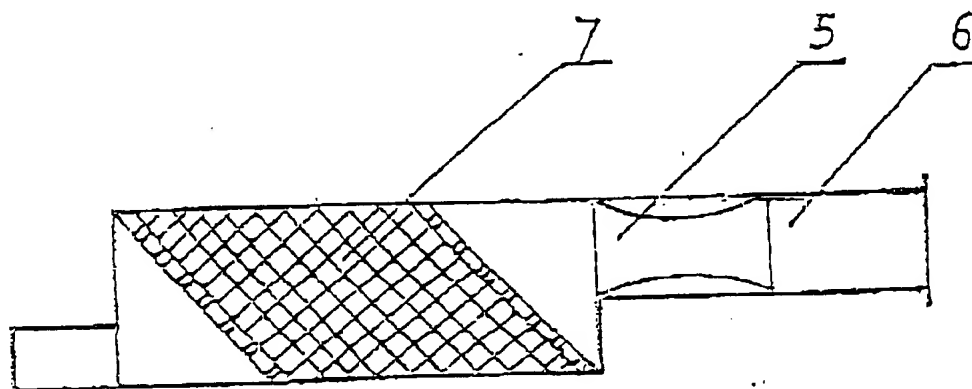


FIG 3

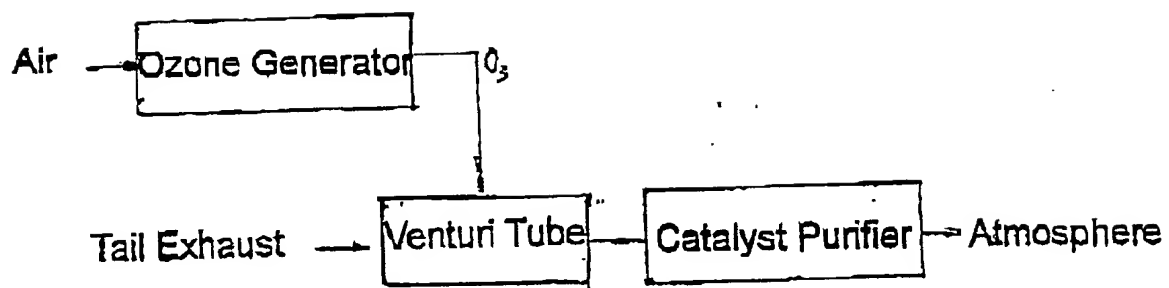


FIG 4